ANSWERS: Crystal ball questions on Level 3 Organic practical

1) Ethyl ethanoate is an ester and is formed from ethanol and ethanoic acid.

Firstly, the ethanol has to be oxidised using an oxidising agent to form the ethanoic acid. Place 1mL of the ethanol into a test tube and add 2mL of dilute H_2SO_4 followed by 1mL of either $KMnO_4$ or $K_2Cr_2O_7$. Place the test tube into a water bath and heat for approx 5 minutes. A colour change will occur of either purple to colourless (with the $KMnO_4$) or orange to green (with the $K_2Cr_2O_7$).

The general equation for the oxidation reaction of alcohol → carboxylic acid is

$$C_2H_5OH \xrightarrow{[O]} CH_3COOH$$

The Redox equation for the reaction is:
Please note that for the organic chemistry exam is will <u>not</u> be necessary to write the balanced redox equation for the oxidation of ethanol

<u>Using Potassium permanganate</u>
reduction half equation: $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$
oxidation half equation: $CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e$
(easiest to balance the oxidation equation using charges as opposed to oxidation numbers)

20 electrons is the lowest common number for 5e and 4e
so, multiply/times reduction half equation x 4: $4MnO_4^- + 32H^+ + \cancel{20e} \rightarrow 4Mn^{2+} + 16H_2O$
and multiply/times oxidation half equation by 5: $5CH_3CH_2OH + 5H_2O \rightarrow 5CH_3COOH + 20H^+ + \cancel{20e}$

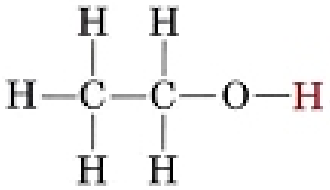
So, the overall balanced redox equation is $4MnO_4^- + 12H^+ + 5CH_3CH_2OH \rightarrow 4Mn^{2+} + 5CH_3COOH + 11H_2O$

<u>Using Potassium dichromate</u>
reduction half equation: $Cr_2O_7 2^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$
oxidation half equation: $CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e$

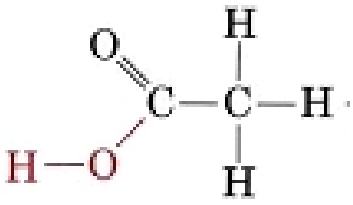
12 electrons is the lowest common number for 6e and 4e
so, multiply/times reduction half equation by 2: $2Cr_2O_7 2^{2-} + 28H^+ + \cancel{12e} \rightarrow 4Cr^{3+} + 14H_2O$
and multiply/times oxidation half equation by 3: $3CH_3CH_2OH + 3H_2O \rightarrow 3CH_3COOH + 12H^+ + \cancel{12e}$

So, the overall balanced redox equation is $2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \rightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$

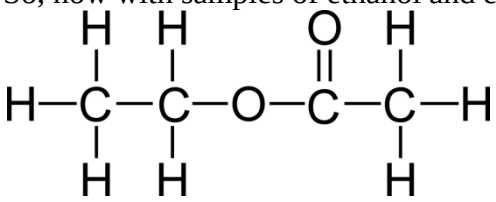
The structural formula for ethanol is



The structural formula for ethanoic acid is



So, now with samples of ethanol and ethanoic acid, the ester ethyl ethanoate can be produced.



The equation for the condensation reaction to form ethyl ethanoate is

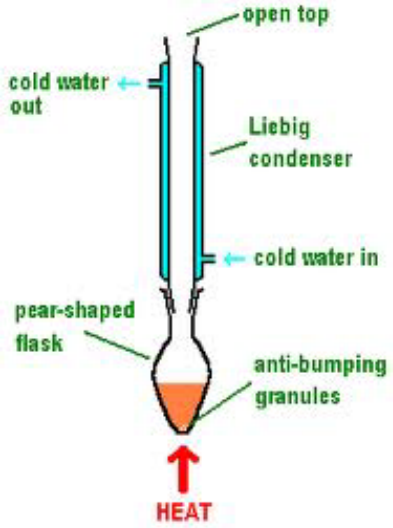
$C_2H_5OH + CH_3COOH \rightarrow C_2H_5COOCH_3$

This is a condensation reaction which is catalysed by H^+ ions. Concentrated H_2SO_4 is both a dehydrating agent and provides the H^+ ions for the reaction. Place 2mL of ethanol in a test tube, add 1mL of pure ethanoic acid followed by a couple of drops of concentrated H_2SO_4. Warm the mixture in a water bath for a few minutes. Then, add the mixture to 15mL of Na_2CO_3 solution, this is to neutralise any excess acid. Once the bubbling of carbon dioxide stops, pour the solution into a boiling tube, the ester layer will be visible on top of the aqueous layer and should have a sweet pear smell.

2) Ethyl ethanoate is an ester and formed from ethanol and ethanoic acid.

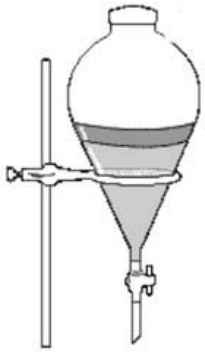
The general equations and structural formula have all been provided in answer 1 (above)

Firstly, set up the Liebig condensor for reflux. Make sure that the cold water tap is on.



Place 10mL of ethanol into a pear shaped flask, add 10mL of acidified $KMnO_4$ or $K_2Cr_2O_7$. Ideally KMnO4 as the colour change is from purple to colourless, resulting in a colourless solution. Add in a couple of anti-bumping granules. Heat the pear shaped flask by either moving a bunsen burner to and fro or allowing the pear shaped flask to rest in a tray of sand placed on a hot plate or a water bath. Allow the mixture to boil and reflux thus fully oxidising the primary alcohol, in this case ethanol to a carboxylic acid, in this case ethanoic acid. Reflux means that as the warm vapours from the ethanol rise into the cold condensor they will condense and fall back into the pear shaped flask, the oxidising agent will cause the ethanol to be oxidised firstly to the aldehyde, ethanal and then full oxidised to the carboxylic acid, ethanoic acid. Because the reaction mixture is continually refluxing then end result will ensure that full oxidation to a carboxylic acid has occured. A change in colour (colours given in answer 1) will indicate that oxidation is complete.

Carry out simple distillation of the reaction mixture and at 118'C collect the distillate, which is ethanoic acid, pour into a conical flask, add 10mL of ethanol and then 1mL of conc H_2SO_4 as a dehydrating agent (see equation in answer 1). Warm the conical flask in a water bath for a few minutes. Pour the resulting mixture into a beaker of aqueous sodium carbonate to neutralise any excess acid. Once the mixture stops bubbling, pour into a separating funnel.



Allow to settle and carefully separate out the top organic layer which is the ester, ethyl ethanoate.

3)

The chart below summaries the oxidation of butanol (primary, secondary and tertiary alcohols)

primary alcohol → *aldehyde* → *carboxylic acid*

butan-1-ol or 2-methylpropan-1-ol → butanal → butanoic acid

secondary alcohol → *ketone*

butan-2-ol → butanone

tertiary alcohol → *no reaction*

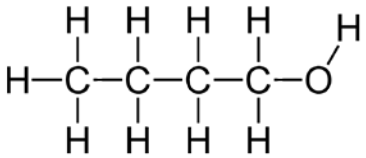
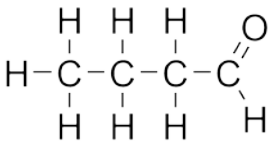
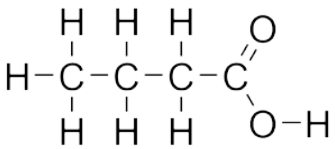
2-methylpropan-2-ol

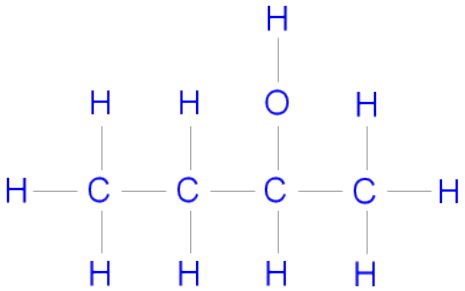
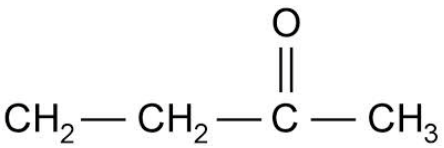
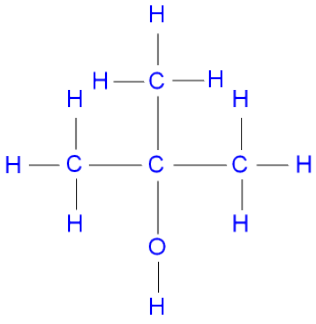
Suitable oxidising agents to use are acidified $KMnO_4$ or $K_2Cr_2O_7$

A suggested procedure is to place 0.5 mL of $KMnO_4$ or $K_2Cr_2O_7$ and 1mL of dilute sulfuric acid into a test tube. Add 1mL of butan-1-ol. Swirl and if necessary heat in a water bath for a few minutes until a colour change occurs; purple → colourless with $KMnO_4$ or orange → green with $K_2Cr_2O_7$

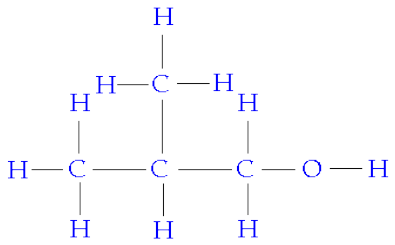
Repeat the procedure for each isomer of butan-1-ol.

The structural formula of reactants and products are

butan-1-ol	butanal	butanoic acid
		

butan-2-ol	butanone	2-methylpropan-2-ol
		

2-methylpropan-1-ol



4)
There are different uses for a Liebig condensor, one is distillation, another is reflux.

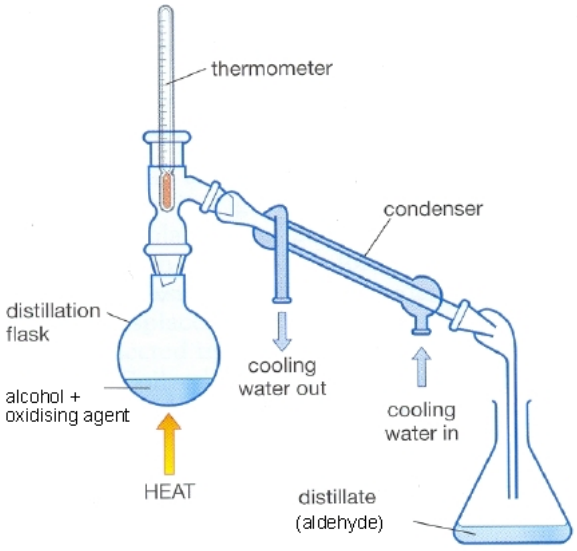
Distillation
Distillation is a liebig condensor arranged horizontally on a pearshaped flask using quickfit apparatus.
Distillation is a process used to separate miscible liquid which have different boiling points.
Partial oxidation of a primary alcohol such as propanol will result in the formation of an aldehyde, propanal.
The aldehyde must be distilled from the solution at its boiling point or the aldehyde will continue to be further oxidised and form propanoic acid.

The equation for the reaction is

$$C_3H_7OH \xrightarrow{[\text{partial O}]} C_3H_6O$$

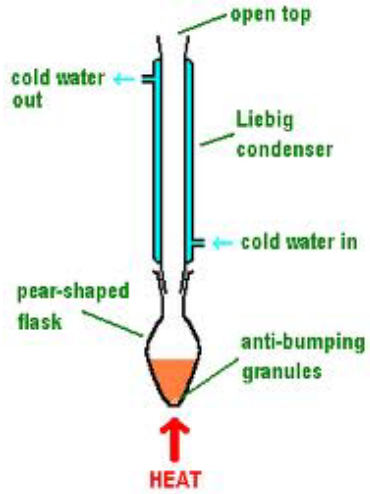
Reagents required are an oxidising agent such as acidified $KMnO_4$ or acidified $K_2Cr_2O_7$
Conditions required are gentle heat for approx 5 mins, this is achieved by having the bunsen on a medium heat and moving it to and fro under the pear shaped flask.
Anti-bumping granules or porcelain chips should be added to the pear shaped flask at the start of the reaction to prevent the reaction mixture boiling over into the Liebig condensor.

See the distillation apparatus below



The way the Liebig condensor works is that it is made up of two tubes, an inner and outer tube. The outer tube is connected to the cold water tap (water in at the bottom and out at the top), therefore the inner tube is kept cool. The warm aldehyde vapour rises from the pear shaped flask and though the condensor, because the inner tube of the condensor is cool the warm aldehyde vapours will condense to form aldehyde liquid which drips down and out of the Liebig condensor and into the conical flask.

Reflux
Reflux is a process whereby a Liebig condensor is arranged vertically on a pearshaped flask using quickfit apparatus, as shown below.



The process of reflux can be used for the full/total oxidation of a primary alcohol eg propanol to a carboxylic acid eg propanoic acid. Reflux is a distillation technique involving the condensation of vapours and the return of this condensate to the pear shaped flask from which it originated. Heating under reflux prevents the aldehyde formed escaping before it has time to be oxidised to the carboxylic acid. This is because the cold water in the outer tube of the Liebig condensor causes the aldehyde vapours in the inner tube to condense and fall back into the pear shaped flask where they will continue to be oxidised.

The equation for the reaction is

$$C_3H_7OH \xrightarrow{[\text{total O}]} C_2H_5COOH$$

Reagents required are an excess of an oxidising agent such as acidified $KMnO_4$ or acidified $K_2Cr_2O_7$
Conditions required are gentle heat for approx 5 mins, this is achieved by having the bunsen on a medium heat and moving it to and fro under the pear shaped flask.
Anti-bumping granules or porcelain chips should be added to the pear shaped flask at the start of the reaction to prevent the reaction mixture boiling over into the Liebig condensor.

The process of reflux should continue until the oxidising agent has changed colour ie purple to colourless for $KMnO_4$ or orange to green for $K_2Cr_2O_7$. Then the apparatus needs to be rearranged for distillation so the the carboxylic acid can be distilled off at the appropriate boiling point.

5) i) <u>ethanamide from chloroethane</u>
Firstly, form ethanol by carrying out a substitution reaction using heat, of the chloroethane and NaOH

$$C_2H_5Cl \xrightarrow{NaOH} C_2H_5OH$$

Then, totally oxidise the ethanol to ethanoic acid using an oxidising agent such as acidified $KMnO_4$ or $K_2Cr_2O_7$

$$C_2H_5OH \xrightarrow{[O]} CH_3COOH$$

Finally, carry out a substitution reaction of ethanoic acid with NH_3 to form the amide

$$CH_3COOH \xrightarrow{NH_3} CH_3CONH_2$$

ii) <u>ethanoyl chloride from propene</u>
Firstly, add water (and some dilute H_2SO_4) to form propanol

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

Then, totally oxidise the ethanol to ethanoic acid using an oxidising agent such as acidified $KMnO_4$ or $K_2Cr_2O_7$

$$C_2H_5OH \xrightarrow{[O]} CH_3COOH$$

Finally, carry out a substitution reaction with PCl_3, PCl_5 or $SOCl_2$ to form the ethanoyl chloride

$$C_2H_5COOH \rightarrow C_2H_5COCl$$